# A Cost Effective Strategy for Extracting Pore Water: Sipper vs. Centrifugation Method

The Department of Defense Environmental Monitoring and Data Quality Workshop

Tetra Tech FW, Inc.
South Florida Water Management District

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# “Modified” Sipper Method

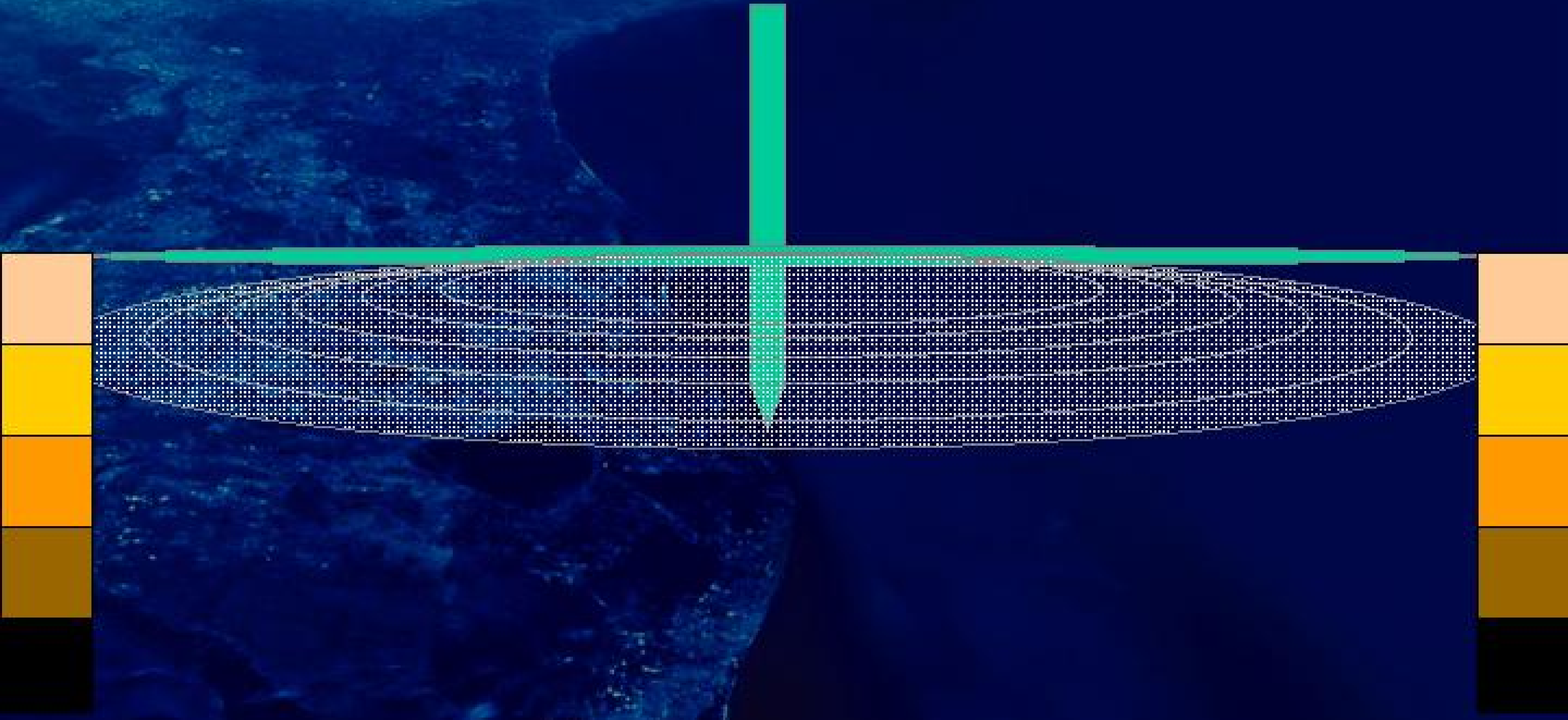
- **Limitations**
  - Sediments perforated by physical or biological channels or conduits, the path of least resistance of pore water flow may be in the vertical rather than the horizontal direction
  - Sample is collected at a constant sediment bulk modulus rather than a constant sediment depth
  - Unable to discriminate contributions from distinct strata

# “Modified” Sipper Method

- **Advantages**
  - Greater pore water sample volume without surface water breakthrough
    - allows for commercial lab analysis and split sampling validation with other methods
  - Large sample volume may average out local microheterogeneities yielding a more representative sample of the system
  - Hands-free sampling with less susceptibility to inadvertent movement of probe during sample collection
  - Teflon construction allows for collection of ultra-clean, ultra-trace Hg and redox-sensitive analytes
  - Consistent placement angle
  - Reproducible sample depth

# Conclusions

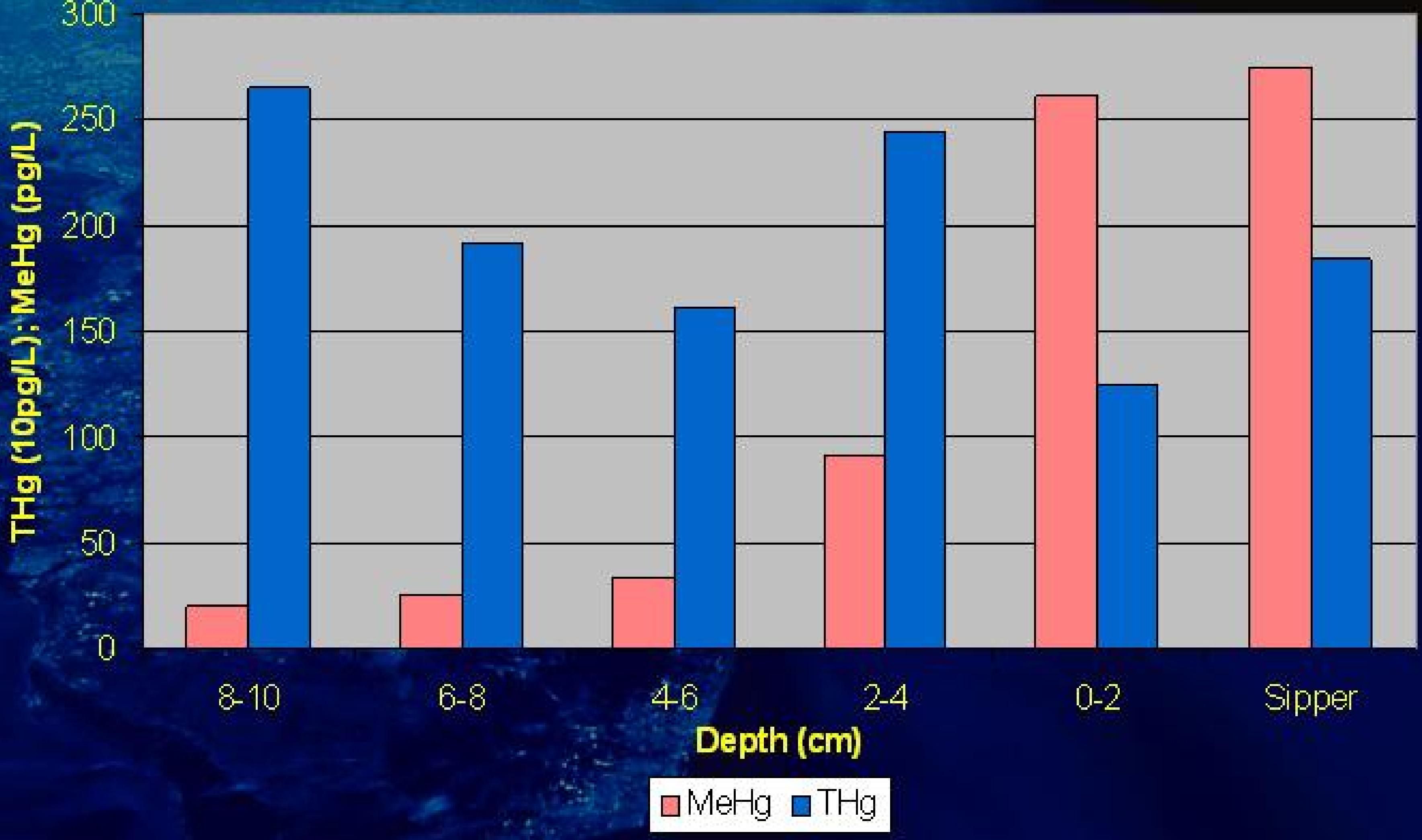
- Soil Physicochemical Stratification vs. Sipper Ellipsoid of Withdrawal



# Conclusions

- **Pore water was easily extracted from three different sites with varying vegetative conditions and in water depths to over 1 meter**
- **Data from three separate sites indicate the "modified" sippers area of withdrawal to be ~ 0-5 cm (+/- 1 cm)**
- **Pore water redox readings recorded on-site showed a substantial difference from surface water redox readings**
  - Pore water redox readings ~ -200 to -300 mv
  - Surface water redox readings ~ -30 to +70 mv
- **Differing sediment types were encountered with minimal variations observed in the results**
- **Sediments with dense emergent vegetative cover (*Sagittaria spp.*, *Pontederia spp.*) with physical or biological channels seem to follow the path of least resistance which may be in the vertical rather than horizontal direction**

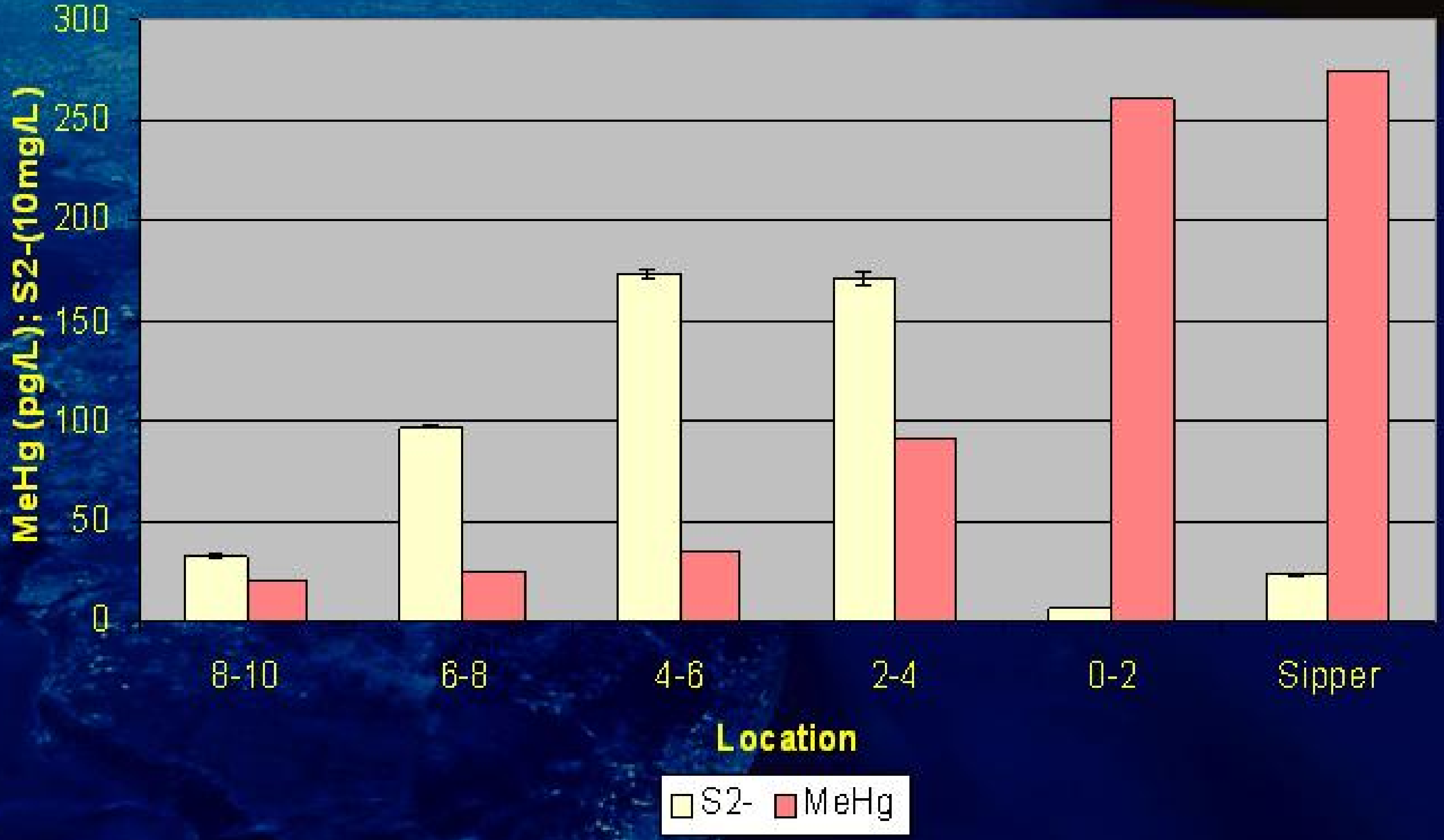
# MeHg & THg Profile - Site C1C



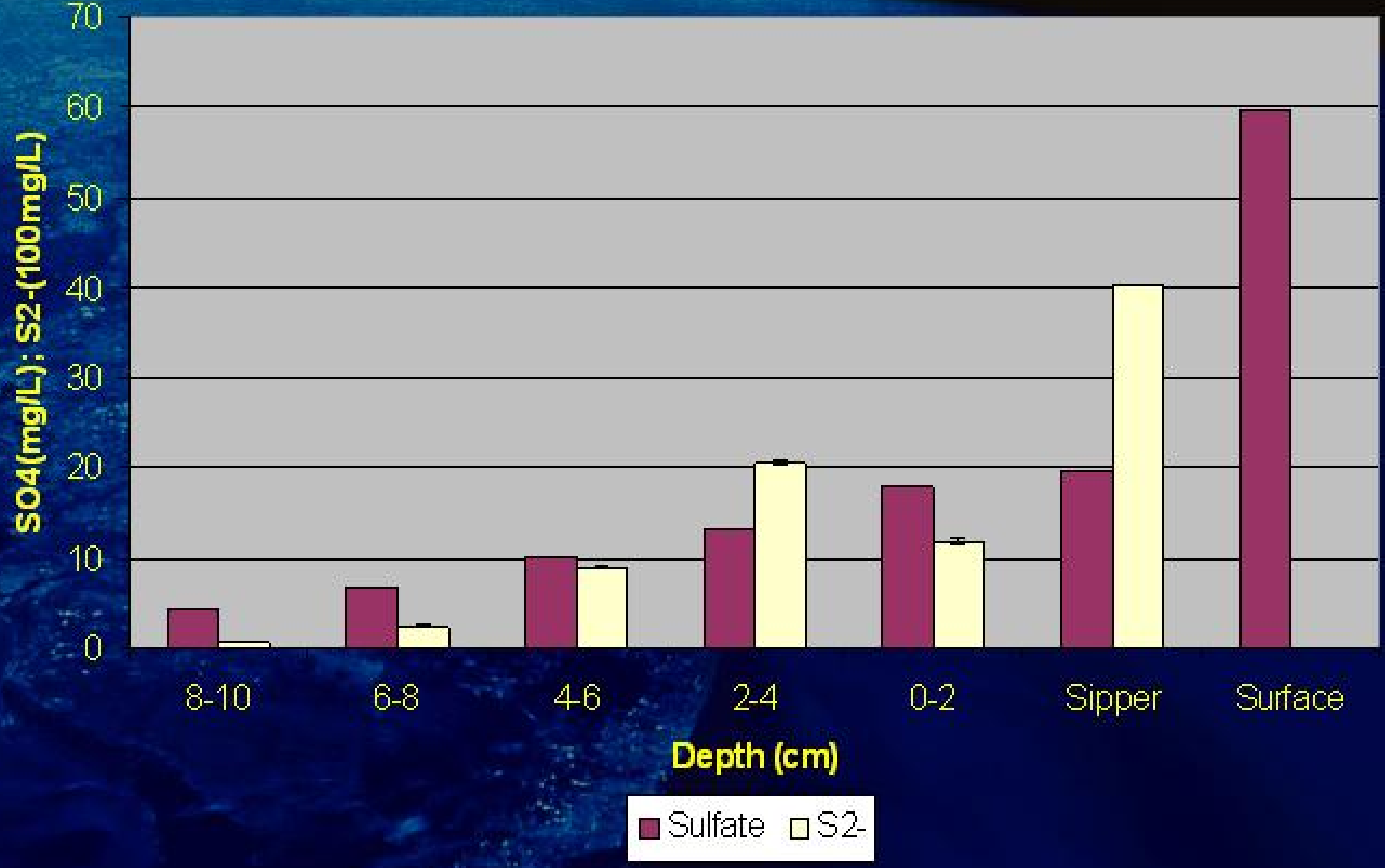
# In Summary

- Preliminary data suggest the "modified" sipper collection method is a simple, cost effective, and reliable *in situ* method for routine monitoring of pore water chemistry
- Pore water yield is sufficient for multiple constituent analysis by commercial laboratory
- Reliable method for collection of pore water for Ultra-Trace, Ultra-Clean Hg species and redox sensitive analytes in varied Everglades sediments
- Centrifugation is a good method for determining pore water chemistry within distinct strata, although is not a cost effective method for routine pore water monitoring

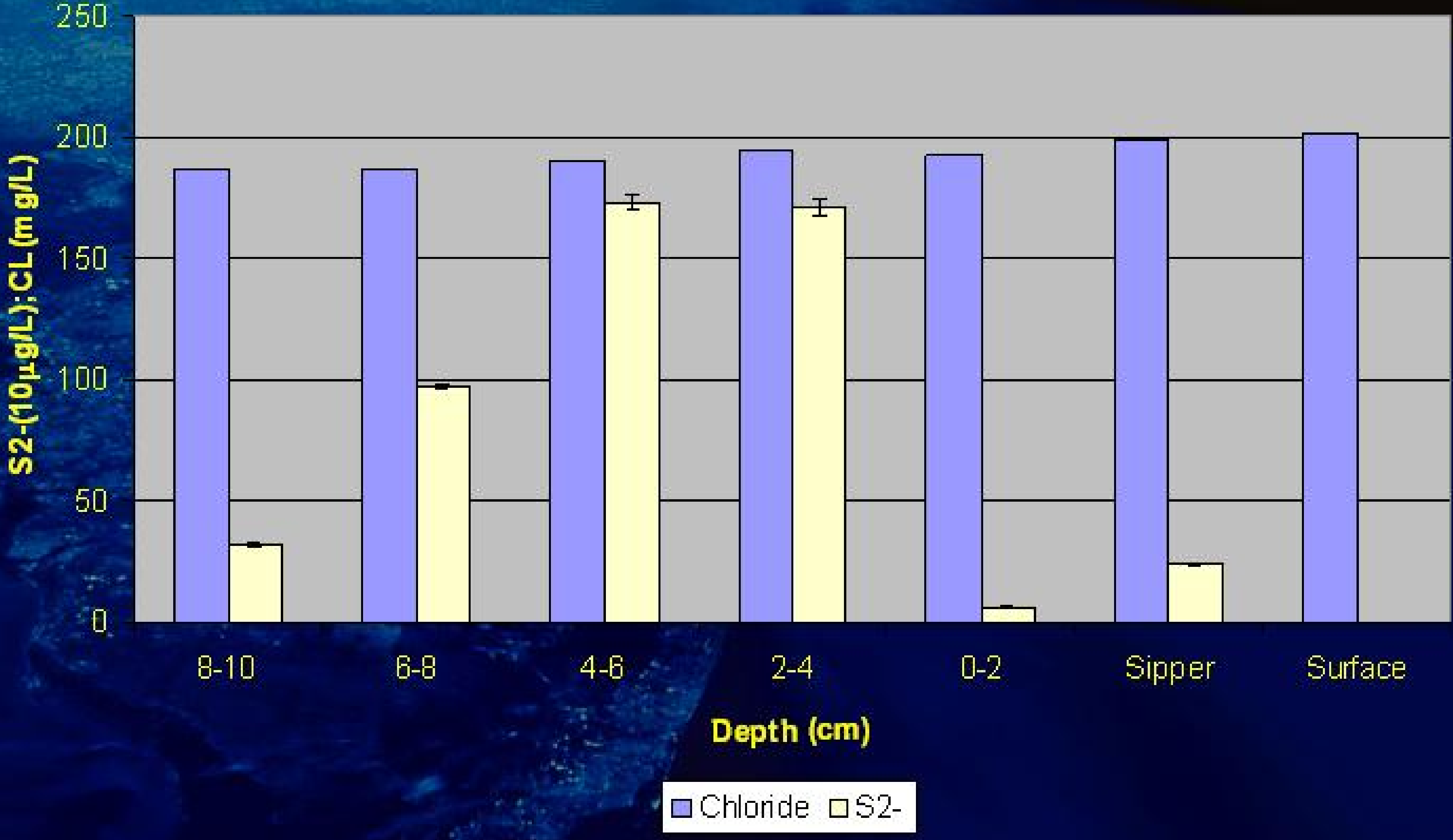
## MeHg & S2- Profile - Site C1C



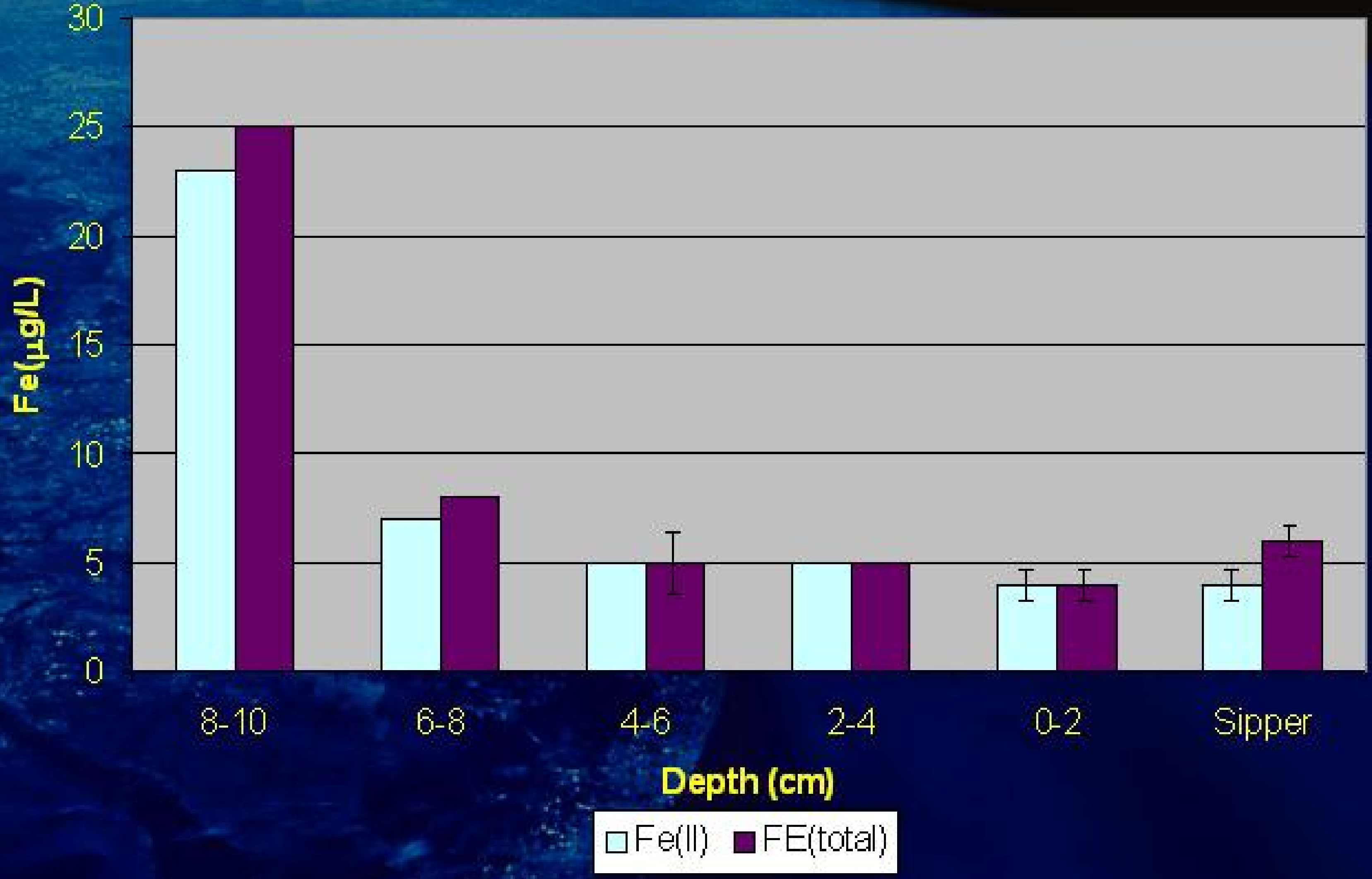
# SO4 & S2- Profile - Site C3C



# S2- & CL Profile - Site C1C

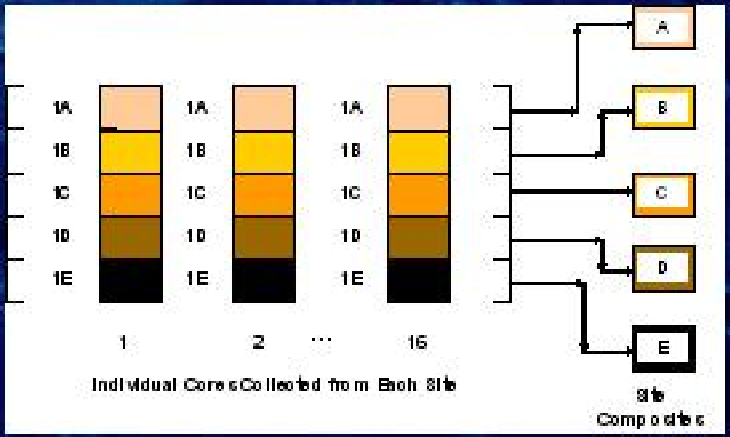


# TFe & Fe(II) Profile - Site C1C



# Validation Study

- Data obtained from the sediment centrifugation method and "modified" sipper method were compared in an attempt to locate the "modified" sippers area of withdrawal

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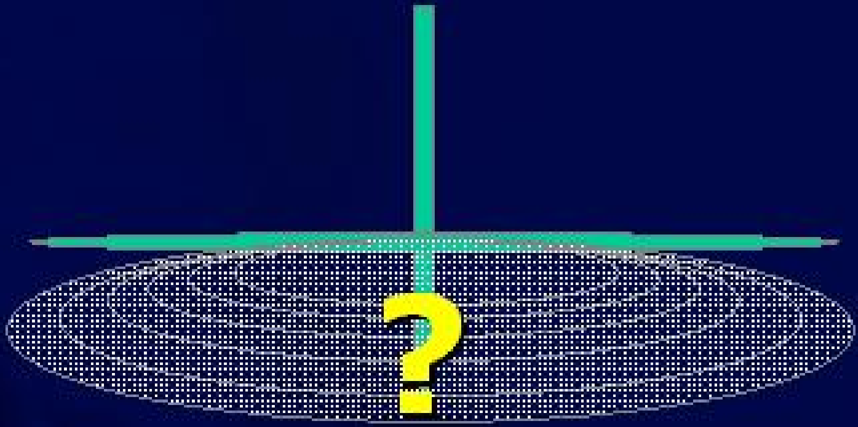
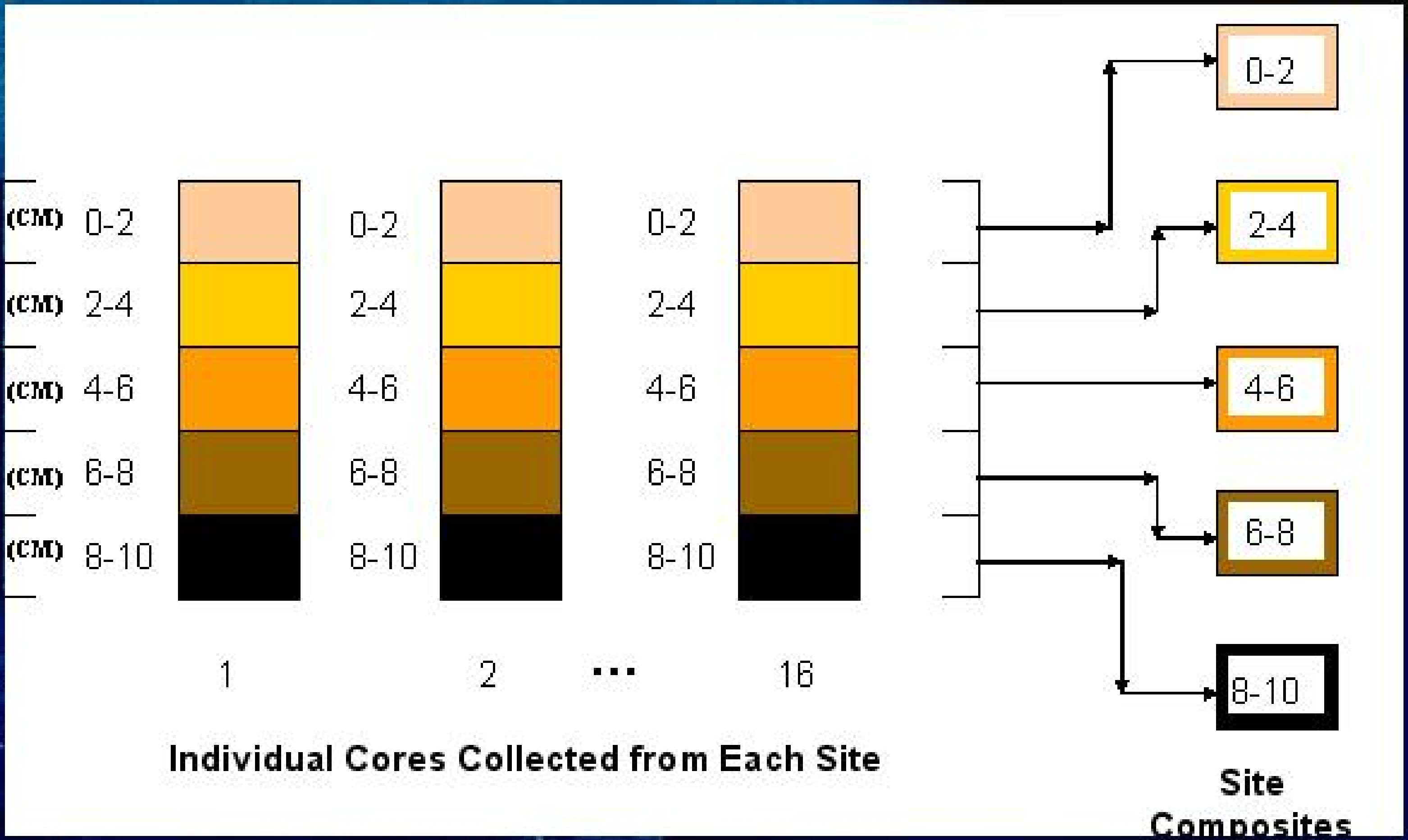


# Validation Study

- **"Modified" Sipper Method**
  - Subsequent to sediment core collection at each of the three sites, pore water via the "modified" sipper method was collected, filtered (0.45µ), and analyzed for pH and redox in the field and TFe, $Fe^{2+}$,$Fe^{3+}$, $S^{2-}$, $SO_4^{2+}$, DOC, CL, Ca, Mg, and TMn by the SFWMD lab
  - Samples to be analyzed for THg and MeHg were shipped to Frontier Geosciences

# Validation Study



# Validation Study

- Sediment cores were cut into 5 distinct sediment strata under anoxic conditions (nitrogen) inside of a glove box
- Each strata (0-2, 2-4, 4-6, 6-8, and 8-10 cm) was centrifuged, filtered (0.45μ), and subsequently analyzed for pH, redox, TFe, $Fe^{2+}$,$Fe^{3+}$, $S^{2-}$, $SO_4^{2+}$,DOC, CL, Ca, Mg, and TMn by the SFWMD lab
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# Validation Study

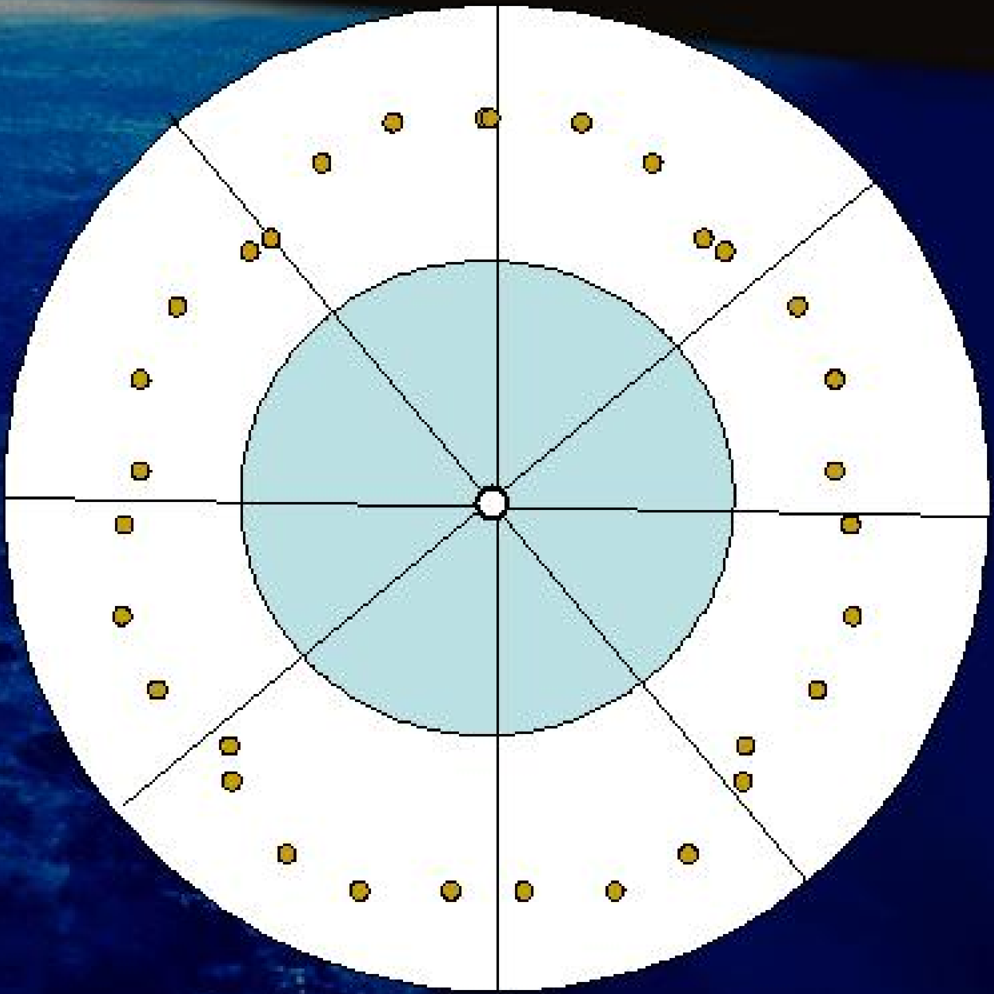


Diagram 1. Placement of Corer For Sediment Collection

# Validation Study

- Sediment cores were collected from three separate sites with varying sediment and vegetative conditions
- Sediment cores were collected, prior to pore water collection via the "modified" sipper method, from the perimeter of the emplaced sipper disc
- Cores were immediately transported to the on-site portable laboratory
- Cores were extruded within 2 hours of collection

# Validation Study

- **Soil Centrifugation Method**
  - Construction trailer and generator were set up to act as a temporary on-site laboratory
  - Portable Laboratory was outfitted with a continuos nitrogen supply, centrifuge, glove box, soil core extruder, vacuum pumps, and associated equipment required for filtering and preservation of samples

# Validation Study

- A portable laboratory was setup at STA-2 for extraction of pore water via centrifugation from soil cores collected
- Results were compared against pore water analytical results obtained by the modified sipper method

# "Modified" Sipper Method

- Redox/pH is continually monitored under anoxic conditions using in-line flow-thru probes between the sample collection tubing and the sample collection bottle
- Provides a continuous verification of the absence of surface water breakthrough and thus sample validity

# “Modified” Sipper Method

- Handle is stiffened with a series of cross bars that act as a platform for a set of equally distributed weights
- Weights are used to ensure that uniform pressure is applied on the sediment to seal off the surface water/sediment interface and to prevent surface water breakthrough

# "Modified" Sipper Method

- One-meter long PVC handle has been added to facilitate probe placement into the subsurface soil/sediment layer
- Handle is affixed to the top of the disk with a series of circular mounts

# "Modified" Sipper Method

- Sipper probe is inserted through the disk, placed to the desired depth, and locked to ensure proper deployment

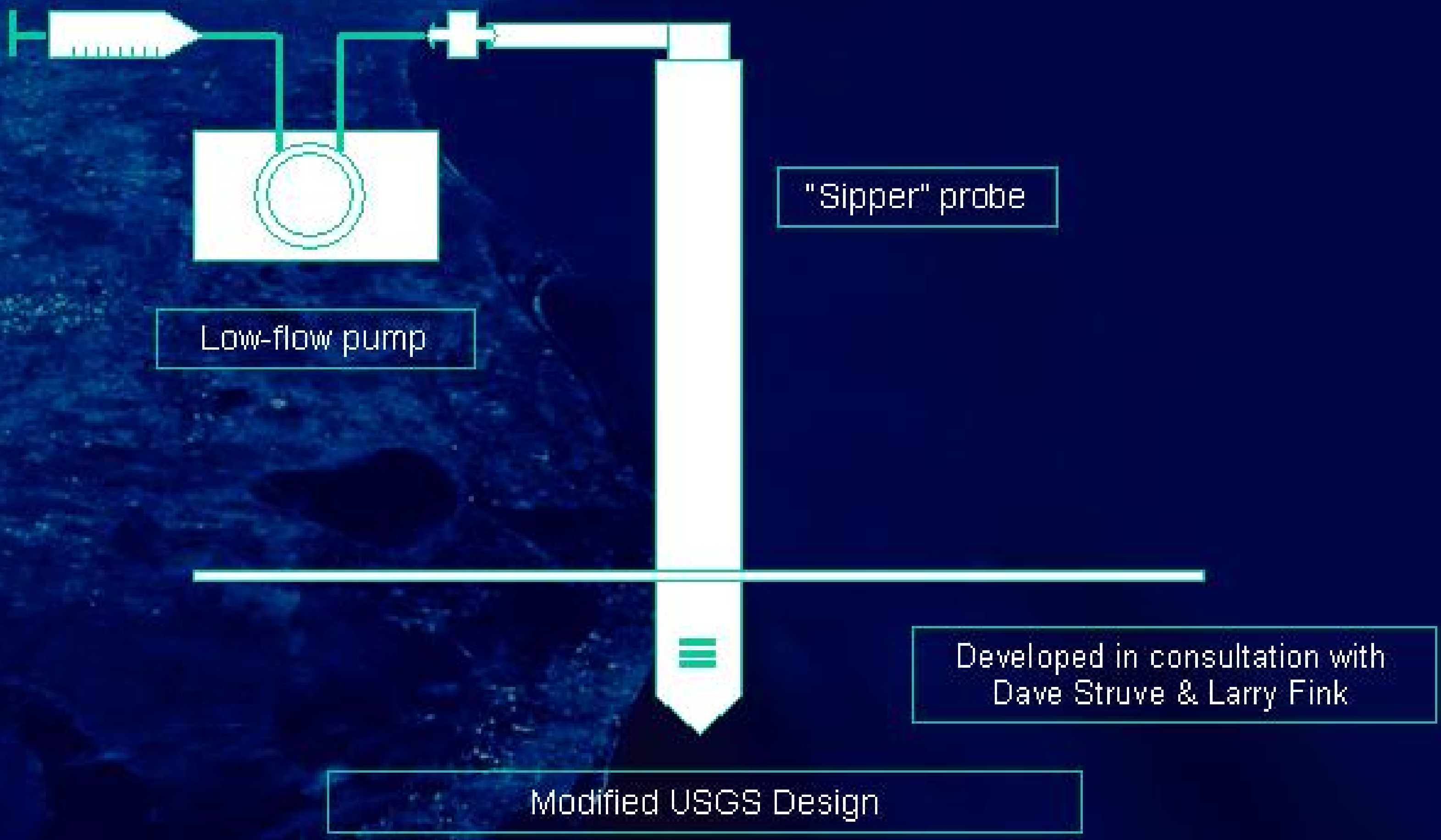
# “Modified” Sipper Method

- Modifications were made to the original USGS *in situ* sipper design for ultra-clean collection of ultra-trace mercury species analytes in pore water

- Addition of a 0.75 m diameter x 0.025 m thick molded disk composed of polyethylene “starboard” through which a 0.025 m hole has been drilled through the center to accommodate the Teflon barrel of the sipper probe

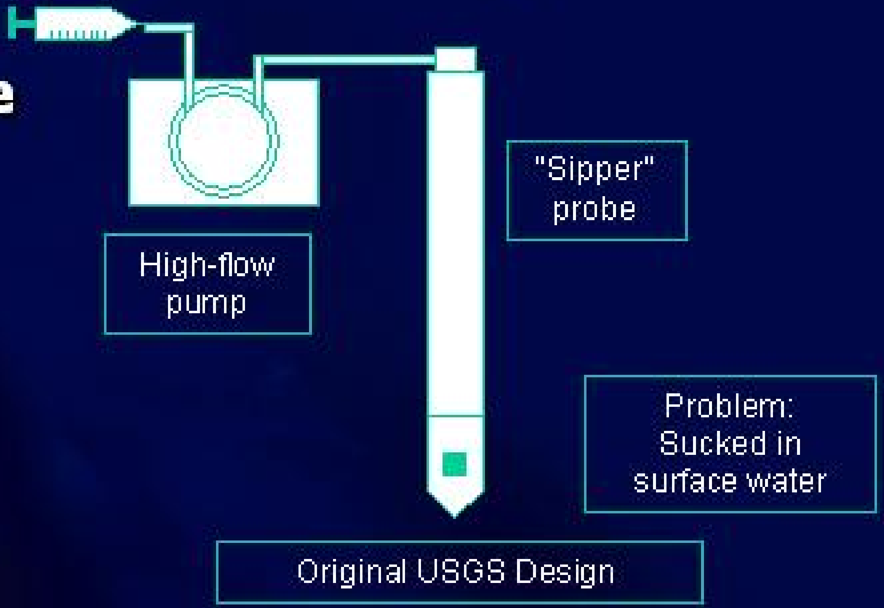
# *In situ* "modified" Sipper

## Designed for ultra-clean collection of ultra-trace mercury species analytes in pore water



# Original USGS *in situ* Sipper

- *In-situ* pore water collection method
- Pore water collection via a pre-cleaned (for ultra-trace Hg analysis) slotted Teflon probe ("sipper") deployed to desired depth
- Capable of collecting volumes of pore water up to 150 ml per deployment
- Difficult to reproduce sample depth in varying sediments
- Uncertainty of stratum collected
- Uncertainty of surface water intrusion
- Limited use in deeper water



# Pore Water Collection Pilot Study

- A Pilot Study was necessitated by the absence of a cost effective, practical on-site method of valid pore water collection under oxygen-free conditions
- The study was undertaken to validate an alternative method ("modified" sipper) versus the soil core centrifugation method
- Centrifugation and modified sipper pore water extraction method advantages and limitations were determined by the pilot study

# Why Do We Need Pore Water Monitoring Capability?

- It was hypothesized (Fink, 2002) that pore water sulfide would eventually build up to levels that would inhibit Hg methylation
- Monitoring both the increase of sulfide and the decrease of MeHg in Cell 1 pore water over time would verify that the mitigative measure was working
- Unfortunately, there was no readily implementable pore water sampling method available that was valid for both ultra-trace mercury and sulfide outside the research community

# Why Do We Need Pore Water Monitoring Capability?

- Previous studies in the Everglades indicated that high pore water sulfide concentrations were associated with low pore water MeHg concentrations (Gilmour et al., 1999)
- Initiating flow-through operations in Cell 1 with agricultural runoff would increase the sulfate loading rate per unit area, thereby increasing sulfide concentrations in the anaerobic surficial sediments

# Why Do We Need Pore Water Monitoring Capability?

- STA-2 Cell 1 experienced a MeHg anomaly following first-flooding (4.2 ng/L peak unfiltered MeHg in 9/00) and re-flooding (7.8 ng/L in 10/01; 20 ng/L in 8/02)
- Unlike Cells 2 and 3, the first-flush MeHg problem in Cell 1 persisted long enough to bioaccumulate in the aquatic food chain

# Historical Overview

The 1994 Everglades Forever Act required the South Florida Water Management District to construct, among other things, a series of Stormwater Treatment Areas (STAs), otherwise known as constructed wetlands to act as a buffer between the Everglades Agricultural Area and the Everglades to the south. The primary function of an STA is to remove excess nutrients (particularly phosphorus) from the water column through a number of physical and biological processes.

# Presentation Outline

- Historical Overview - The 1994 Everglades Forever Act
- Why do we need pore water monitoring capability?
- Pore Water Collection Pilot Study
- Pore Water Study Implementation
- Conclusions
- Advantages and Limitations
- Summary

# Presenters & Authors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